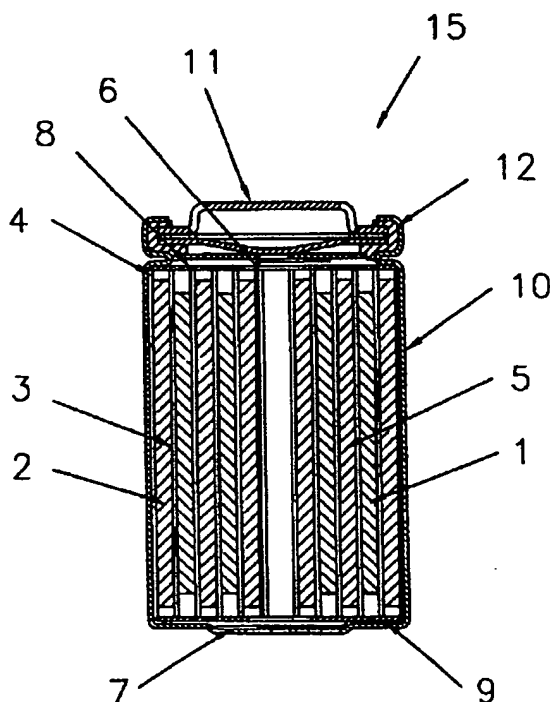(72) ZHONG, Qiming, CA
(71) MOLI ENERGY (1990) LIMITED, CA

(51) Int.Cl.^{6} H01M 10/26

(54) ACCUMULATEURS AUX IONS DE LITHIUM FAISANT APPEL A DES ANODES DE GRAPHITE TRAITEES AU BORE ET A DES SOLVANTS INCOMPATIBLES AVEC LE GRAPHITE

(54) LITHIUM ION BATTERIES EMPLOYING BORON TREATED GRAPHITE ANODES AND GRAPHITE INCOMPATIBLE SOLVENTS

(57) Les carbones hautement graphitiques ayant des espacements moyens d_{002} inférieurs à 3,37 Å sont recherchés comme matières anodiques de capacité élevée pour les accumulateurs aux ions de lithium non aqueux rechargeables. Cependant, ces anodes graphitiques sont incompatibles avec certains solvants électrolytiques courants, dont le carbonate de propylène. De manière inattendue, les anodes de carbone graphitique traitées au bore, mais par ailleurs semblables, peuvent être compatibles avec ces solvants. Le traitement au bore peut également être utilisé pour graphitiser encore davantage l'anode de carbone.

(57) Highly graphitic carbons with average d_{002} spacings less than 3.37 Å are desirable as high capacity anode materials for non-aqueous rechargeable lithium ion batteries. However, such graphitic anodes are incompatible with certain common electrolyte solvents, including propylene carbonate. Unexpectedly, boron treated, but otherwise similar, graphitic carbon anodes can be compatible with these solvents. Boron treatment can be additionally used to further graphitize the carbon anode.

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ABSTRACT

Highly graphitic carbons with average d_{002} spacings less than 3.37 Å are desirable as high capacity

anode materials for non-aqueous rechargeable lithium ion batteries. However, such graphitic anodes

5   are incompatible with certain common electrolyte solvents, including propylene carbonate.

Unexpectedly, boron treated, but otherwise similar, graphitic carbon anodes can be compatible with

these solvents. Boron treatment can be additionally used to further graphitize the carbon anode.

LITHIUM ION BATTERIES EMPLOYING BORON TREATED GRAPHITE ANODES AND GRAPHITE INCOMPATIBLE SOLVENTS

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FIELD OF THE INVENTION

This invention pertains to non-aqueous rechargeable lithium ion batteries employing graphitic carbonaceous anodes and electrolyte solvents or solvent combinations which are conventionally
10   considered to be incompatible for use with such anodes. Specifically, it pertains to boron treated graphitic anodes and methods for doing the treating. Also, it pertains to propylene carbonate solvent or solvent combinations which are incompatible with untreated graphitic anodes.

BACKGROUND OF THE INVENTION

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Lithium ion batteries have been available commercially since about 1991 and are enjoying remarkable success in the marketplace. Such batteries are a preferred rechargeable power source for many consumer electronics applications, particularly laptop computers and cellular phones. Lithium ion batteries are characterized by a large energy density (Wh/L) and high operating voltage (typically
20   above 3½ volts). Two different lithium insertion compounds are used which have ample capacity for reversible lithium insertion but have differing lithium insertion potential for the active cathode and anode materials. At this time, a lithium transition metal oxide (eg. $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$) is usually employed as the cathode material and a carbonaceous compound (eg. coke, graphite, hard disordered carbon) is usually used as the anode material. Various lithium salt and non-aqueous solvent
25   combinations are used as the battery electrolyte.

Notwithstanding the present commercial success of such batteries, supply is rapidly catching up to demand, which in turn is putting pressure on manufacturers to reduce price. There is also continued pressure to increase the energy density of the batteries as well. These factors drive a search for less expensive electrode materials with ever larger reversible lithium capacity.

30   Not surprisingly, the cathode material in lithium ion batteries can be quite expensive (particularly $LiCoO_2$). However, certain anode materials can also be quite expensive directly (ie. materials themselves) or indirectly (ie. if used, additional expense is required elsewhere).

For example, speciality carbon products such as graphitized mesocarbon microbeads are commonly used by many in the art. Mesocarbon microbeads (MCMB) are a spherically shaped, carbon

powder of uniform particle size. It is desirable because the particles pack well (allowing high electrode densities), have low surface area (minimizing undesirable chemical reactions), and can also be somewhat less reactive with the electrolytes commonly employed in lithium ion batteries. European patent application number EP 474,183 provides information on some of these aspects of MCMB.

5   However, this speciality product can currently cost of order of $60 US per kg.

As an example of indirect expense, Canadian patent application serial no. 2,134,052 of Fuji Photo Film Ltd. discloses a group of amorphous metal oxides which exhibit reversible capacities for lithium which far exceed the theoretical value of graphite. However, these materials also exhibit an irreversible lithium capacity which far exceeds that of conventional lithium ion anodes. To compensate

10   for this increased loss, it has been proposed in PCT application number WO96/27910 that 'sacrificial' lithium metal be incorporated into the battery on assembly as well. Such an approach however can substantially increase the cost of the battery, even if the amorphous metal oxide itself proves to be relatively inexpensive.

The desire to have inexpensive batteries with the greatest energy density makes low cost, highly

15   graphitic carbons appear particularly attractive as an anode material. There are, for instance, natural and artificial graphites which are relatively inexpensive, pack well, and which are highly graphitic (therefore having reversible capacities for lithium that are close to the theoretical 372 Ah/kg). However, highly graphitic carbons are not as compatible in general with the common non-aqueous solvents used in lithium batteries. Unfortunately, much irreversible reaction can occur between

20   lithiated, highly graphitic carbon and many common non-aqueous solvents, hence leading to a large capacity loss in a lithium ion battery. The article titled 'High voltage, rechargeable lithium batteries using newly-developed carbon for negative electrode material', Journal of Power Sources, 43-44, (1993) pages 233-239, shows examples wherein highly graphitized MCMB can be compatible with a diethyl carbonate (DEC)/ethylene carbonate (EC) solvent based electrolyte but not with a similar diethyl

25   carbonate (DEC)/propylene carbonate (PC) solvent based electrolyte. However, a lesser graphitized MCMB can be compatible with the latter.

The use of highly graphitic carbon anodes can therefore impose undesirable limitations on the choices of electrolyte and hence potentially on cost and other performance factors. It may therefore be advantageous to find a way of removing these limitations.

30   One means of circumventing these limitations was recently identified by SAFT. Graphite most commonly has a hexagonal crystal structure, although a rhombohedral structure is also well known. In European patent application number EP660432, SAFT disclose that lithiated graphites, whose structural makeup is greater than 10% rhombohedral, can resist exfoliation in solvents such as PC, and hence is more compatible therewith.

Other carbons known in the art are the coke or coke-like carbons, which are characterized by a relatively low degree of graphitization. While it seems that there is no clear defining point in the art which distinguishes coke from graphite, roughly speaking, cokes can be defined as disordered graphitic carbons which are characterized by average d_{002} spacings greater than about 3.37 Å (as determined from

5   x-ray diffraction patterns). On the other hand, 'graphites' are characterized by average d_{002} spacings less than about 3.37 Å. 'Fully' graphitized carbon is characterized by an average d_{002} spacing of 3.348 Å.

A great deal of work has been reported on in the art pertaining to carbons or precursors thereof which have been reacted with various boron containing compounds to produce improved carbonaceous

10   anode materials. However, it appears that much of this work has been performed on fairly disordered carbons and at relatively low reaction temperatures, therefore resulting in fairly disordered graphitic carbon anode end products (eg. coke or coke-like carbons). Thus, heretofore, it appears that highly graphitic, boron treated carbons have not been used in combination with solvents which are normally incompatible with highly graphitic carbons.

15   For instance, in European patent application number EP561372, Matsushita prepares anode materials by mixing various acids, including boric acid (H_3BO_3), with pitch-based artificial graphite and heating the mixtures at temperatures up to 3000°C. It is unclear how graphitic these product anode materials were. Regardless, battery testing was performed in test cells with electrolytes consisting of ethylene carbonate and dimethoxyethane solvents, a solvent combination which is normally compatible

20   with highly graphitic carbons.

Further, in European patent application number EP565273, Sanyo prepares anode materials by mixing and reacting boron containing compounds with pitch coke at temperatures up to 3000°C. These product anodes are not highly graphitic since it is indicated therein that the embodiments of that invention should have a d_{002} value greater than 3.37 Å.

25   Still further, in U.S. Pat. No. 5,498,493, Moli Energy (1990) Ltd. discloses boron substituted carbon anodes, prepared via CVD methods at 900°C, which have very high lithium capacity. The product anodes can have reversible capacities of 1.18 moles of lithium per unit of $(B_{0.17}C_{0.83})_6$, equivalent to about 446 Ah/kg. These product anodes can be successfully used with electrolyte solvents (eg. propylene carbonate) which are normally incompatible with highly graphitic, lithiated carbon.

30   However, as shown therein, these product anodes are not highly graphitic, having d_{002} values greater than 3.37 Å.

Finally, in Japanese published patent application number JP05-251080, Matsushita prepares anode materials by mixing and reacting boron containing compounds with 'natural graphite' at temperatures only up to 1000°C. As indicated therein, anode materials were tested in batteries

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consisting of propylene carbonate and dimethoxyethane solvents, a combination which is not normally compatible with highly graphitic carbons. However, the unreacted 'natural graphite' itself was also tested in the same electrolyte and was compatible therewith, indicating that the unreacted 'natural graphite' actually had a relatively low degree of graphitization (ie. coke-like). Also, the unreacted

5   'natural graphite' only exhibited about 210 mAh/g of reversible lithium capacity, which is also indicative of a relatively low degree of graphitization (ie. coke-like). After reacting the 'natural graphite' with boron compounds at only 1000°C, a temperature generally too low to effect significant graphitization, there was an apparent improvement in reversible capacity (ie. up to 300 mAh/g), but no apparent improvement in irreversible capacity (ie. remaining at about 40 mAh/g). The reacted

10   'natural graphite' anodes therefore exhibited substantially lower capacities than than the aforementioned boron substituted carbons with d_{002} values greater than 3.37 Å.

It has, however, long been known in the art that carbonaceous materials can nonetheless be graphitized more easily when treated or reacted with boron containing compounds at suitably elevated temperatures, eg. above about 2500°C. For example, the boron atoms in boron-doped pyrolytic

15   graphite are mentioned as acting like graphitization 'catalysts' on page 227 of 'Chemistry and Physics of Carbon, edited by P.L. Walker Jr., Vol. 2, 1966, Marcel Dekker, Inc. New York.

SUMMARY OF THE INVENTION

20   Graphitic carbons with average d_{002} spacings less than about 3.37 Å exhibit a high reversible capacity for lithium and are thus desirable anode materials for non-aqueous lithium ion batteries. Unfortunately however, while some irreversible reaction occurs between any lithiated carbon anode and the electrolyte solvent in a lithium ion battery (commonly referred to as passivation reaction), the reaction between lithiated graphites and some electrolyte solvents can be excessive and/or destructive,

25   hence making such solvents incompatible with lithiated graphite.

For instance, the capacity of a lithium ion battery is limited in part by the amount of lithium contained therein. Ideally therefore, the amount of lithium consumed by irreversible reactions is minimized. If too much lithium is consumed as a result of irreversible reaction between a lithiated graphite anode and the electrolyte solvents, it isn't possible to obtain a high capacity battery. However,

30   it is not uncommon for certain graphitic carbon/solvent combinations to consume the equivalent of well over 100 mAh worth of lithium per gram of graphitic carbon. Such levels are generally impractical for use in lithium ion batteries.

Further, some solvents can insert into graphitic carbons along with lithium (eg. co-intercalate) resulting in significant expansion of the crystal lattice of the graphitic carbon and causing destructive

exfoliation thereof. Hence, such solvents are also not considered compatible with lithiated graphite.

Certain electrolyte solutions are nonetheless reasonably compatible with lithiated graphitic carbons, and thus it is possible to construct lithium ion batteries which use graphitic carbon anodes and which show acceptable capacity. However, since many other common lithium battery solvents are

5   incompatible therewith, the choice of electrolyte solvents has historically been limited. It therefore has not been possible to obtain many of the advantages associated with these common solvents in combination with the capacity advantages of a graphitic anode.

It has been discovered that boron treatment of a graphitic carbon anode in a lithium ion battery can make it possible to employ common lithium battery electrolyte solvents which are not

10   conventionally considered compatible therewith. That is, boron treated graphite carbon anodes having an average d_{002} spacing less than 3.37 Å can be used in combination with a non-aqueous solvent which is compatible with a lithiated coke (ie. a lithiated first graphitic carbon having an average d_{002} spacing more than 3.37 Å), but which is incompatible with a common, untreated lithiated graphite (ie. a lithiated second graphitic carbon having an average d_{002} spacing less than 3.37 Å.)

15   The boron treated graphitic carbon in the battery anode can be a flaky graphite, particularly an artificial flaky graphite. It is not necessary for the crystalline structure of the boron treated graphitic carbon to contain a substantial rhombohedral phase component. Indeed, the crystalline structure of the boron treated graphitic carbon can not only be less than 10% rhombohedral phase, but can be essentially all hexagonal phase.

20   The non-aqueous solvent which is incompatible with untreated graphite carbon anodes can be propylene carbonate. The complete electrolyte can additionally comprise ethylene carbonate and diethyl carbonate solvents and $LiPF_6$ as a lithium salt.

In a battery of the invention, the irreversible lithium capacity of the boron treated graphitic carbon anode can be less than about 100 mAh/g. The anode can also exhibit some reversible lithium

25   capacity at about 1.2 V versus Li/Li^+. Boron treated graphites may contain up to 2.3 atomic percent boron (based on the known solubility limits for boron in carbon).

A boron treated graphitic carbon having an average d_{002} spacing less than 3.37 Å can be prepared for use as an anode in a lithium ion battery of the invention simply by heating a suitable mixture of a carbonaceous compound and a boron containing compound under an inert atmosphere.

30   The initial carbonaceous compound used can be a coke, or alternatively can already be a graphite having an average d_{002} spacing less than 3.37 Å. In particular, the initial carbonaceous compound can be a natural or artificial graphite which is essentially hexagonal phase. The boron treated graphitic carbon anode product can have an average d_{002} spacing between 3.37 Å and 3.35 Å.

Suitable boron containing compounds for purposes of the preparation are B_4C, H_3BO_3, and

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particularly B_2O_3. The atomic ratio of boron to carbon in the mixture is preferably less than 0.05, and more preferably between about 0.01 to 0.02. The preparation temperature can be above about 2200°C and can take about 30 minutes.

Aside from allowing the use of otherwise incompatible solvents in the battery electrolyte, an additional benefit of the method of the invention is that the carbon anode material is graphitized more readily during the boron treatment. In other words, a given degree of graphitization in a product anode can be achieved more easily when the starting carbonaceous compound is graphitized in the presence of a boron containing compound (ie. lower temperature and/or less heating time required). This can be a significant advantage in the overall preparation of the anode material.

BRIEF DESCRIPTION OF THE DRAWINGS

The following Figures have been provided to illustrate certain aspects of the invention, but these should not be construed as limiting in any way.

Figure 1 depicts a cross-sectional view of a conventional cylindrical spiral-wound lithium ion battery.

Figure 2 depicts the voltage over the first 1½ cycles of the coin cell of Comparative Example 1 as a function of charge per gram of the graphite carbon electrode.

Figure 3 depicts the voltage over the first 1½ cycles of the coin cell of Comparative Example 2 as a function of charge per gram of the graphite carbon electrode.

Figure 4 depicts the voltage over the first 1½ cycles of the coin cell of Comparative Example 3 as a function of charge per gram of the graphite carbon electrode.

Figure 5 depicts the voltage over the first 1½ cycles of the coin cell of Inventive Example 1 as a function of charge per gram of the graphite carbon electrode.

Figure 6 depicts the voltage over the first 1½ cycles of the coin cell of Inventive Example 2 as a function of charge per gram of the graphite carbon electrode.

Figures 7a, b, c, and d show the x-ray diffraction profiles of the graphitic carbonaceous electrodes used in the coin cells of Comparative Example 2, Comparative Example 3, Inventive Example 1, and

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Inventive Example 2 respectively.

Figure 8 depicts the voltage over the first 1½ cycles of the coin cell of Illustrative Example 2 as a function of charge per gram of the graphite carbon electrode.

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DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS OF THE INVENTION

Methods for boron treating graphitic carbonaceous materials are already known in the art. For instance, boron treated graphites have conventionally been prepared by appropriately heating a mixture

10   of a suitable carbonaceous compound powder and a suitable boron containing compound under an inert atmosphere. Such boron treated graphites have long served as oxidation resistant graphites for use in other unrelated applications.

The starting carbonaceous compound could be a coke (which can be graphitized as well as boron treated during by the heating) or, alternatively, the starting carbonaceous compound could

15   already be a graphite (ie. already having an average d_{002} spacing less than 3.37 Å). Relatively inexpensive and abundant sources for the starting carbonaceous compound powder are preferred of course. Suitable carbonaceous compounds include both natural and artificial flaky graphites. Suitable choices for the boron containing compound in the mixture include B_2O_3, B_4C, and H_3BO_3 amongst others.

20   An intimate mixture of the boron containing compound and the carbonaceous compound powder is then prepared and the compounds are subsequently reacted together by heat treating under an inert atmosphere. Conventional temperatures and heating times are used for the reacting (eg. temperatures above about 2200°C and heating times of about 30 minutes). Varying provisions may be needed to remove by-product gases and to maintain the inert atmosphere depending in part on the

25   choice of boron containing compound.

The ratio of the ingredients in the mixture is such that the atomic ratio of boron to carbon is preferably less than about 0.05. Higher ratios are not expected to provide any additional advantage with regards to electrolyte compatibility nor with regards to ease of graphitization. Instead, higher ratios can result in the formation of boron carbide which is undesirable. From existing phase diagrams,

30   the amount of boron which is soluble in carbon is a maximum of about 2.3% at 2300°C. Thus, this may represent a maximum theoretical limit for an advantageous boron/carbon atomic ratio. However, due to losses of reactant and/or incomplete reaction therewith, it may desirable in practice to use a modest excess of boron in the mixture (eg. up to a ratio of about 0.05). Nonetheless, a suitable atomic ratio for boron to carbon in the mixture is between about 0.01 to 0.02.

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Unlike the prior art method disclosed in the aforementioned European patent application number EP660432, it is unnecessary to have a substantial amount of rhombohedral phase present in the product graphite to obtain the electrolyte compatibility advantages of the invention. Hence, it is also unnecessary in the starting carbonaceous compound. Accordingly, the crystalline structure of the

5 carbonaceous compound can be less than 10% rhombohedral phase, and in fact can be essentially hexagonal phase.

After suitable treatment, the boron treated graphitic carbonaceous powder is ready for use in a battery of the invention. Other than the inventive combination of anode and electrolyte solvent, the construction of such batteries can be conventional. Commercial lithium ion batteries come in a variety

10 of sizes and formats, including coin cell and prismatic constructions. Figure 1 shows a cross-sectional view of a typical cylindrical spiral-wound battery lithium ion battery. Therein, a jelly roll 4 is created by spirally winding a cathode foil 1, an anode foil 2, and two microporous polyolefin sheets 3 that act as separators.

Cathode foils for the jelly-roll are prepared by applying a mixture of a suitable powdered cathode

15 material, such as $LiCoO_2$, a binder, and a conductive dilutant onto a thin aluminum foil. Typically, the application method first involves dissolving the binder in a suitable liquid carrier. Then, a slurry is prepared using this solution plus the other powdered solid components. The slurry is then coated uniformly onto the substrate foil. Afterwards, the carrier solvent is evaporated away. Generally, both sides of the aluminum foil substrate are coated in this manner and subsequently the cathode foil is

20 calendered.

Anode foils are prepared in a like manner except that the boron treated graphitic carbon powder prepared as described above (typically about 20 micron size) is used instead of the cathode material and thin copper foil is usually used instead of aluminum. Anode foils are often slightly wider than the cathode foils in order to ensure that anode foil is always opposite cathode foil.

25 The jelly roll 4 is inserted into a conventional battery can 10. A header 11 and gasket 12 are used to seal the battery 15. The header may include safety devices if desired (eg. overpressure vent, positive temperature coefficient device, and/or a pressure activated electrical disconnect device). The external surface of the header 11 is used as the positive terminal, while the external surface of the can 10 serves as the negative terminal.

30 Appropriate cathode tab 6 and anode tab 7 connections are made to connect the internal electrodes to the external terminals. Appropriate insulating pieces 8 and 9 may be inserted to prevent the possibility of internal shorting.

Prior to crimping the header 11 to the can 10 in order to seal the battery, a desirable non-aqueous electrolyte 5, which comprises a non-aqueous solvent that is incompatible with common lithiated

graphite powders, is added to fill the porous spaces in the jelly roll 4. One such solvent is propylene carbonate (PC). The electrolyte can include common lithium salts such as $LiPF_6$ or $LiBF_4$ and can additionally include other desirable non-aqueous solvents (eg. linear and/or cyclic carbonates solvents such as diethyl carbonate (DEC) and ethylene carbonate (EC)).

5   The header 11 is then crimped to the can 10. Lastly, an electrical conditioning step involving at least a single charging of the battery is usually performed next as part of the assembly process.

The following non-limiting Examples are representative of aspects of the invention.

10   **Comparative Example 1**

A laboratory coin cell was assembled and electrically tested to show the electrochemical properties of a conventional lithiated graphite powder in a compatible non-aqueous electrolyte.

The carbon powder used was a commercially available artificial flaky graphite denoted KS15

15   (a product of Lonza). The electrolyte employed was 1 M $LiPF_6$ salt dissolved in a mixture of ethyl methyl carbonate (EMC), EC, and DEC solvents in a volume ratio of 50/30/20 respectively.

The conventional KS15 graphite powder was used as a cathode and lithium metal was used as the anode in the laboratory coin cell in order to determine the electrochemical properties. Coin cell construction was similar to that described in J.R. Dahn et al., Electrochimica Acta, 38, 1179 (1993).

20   The test electrode comprising the KS15 graphite was fabricated in a manner similar to that used for commercial lithium ion battery anodes. That is, a mixture of the KS15 graphite powder, polyvinylidene fluoride binder, and Super S carbon black (trademarked product of Ensagri) conductive dilutant in a weight ratio of 85/10/5 respectively was applied on one side of a thin copper foil and then compacted mechanically.

25   The laboratory coin cell was then cycled 1½ times (ie. lithium was electrochemically inserted, removed, and inserted again into the KS15 electrode) at 21 °C, over a voltage range between 0 and 2 volts versus Li/Li^+, and at low rate (approximately C/40). Figure 2 depicts the voltage over these first 1½ cycles as a function of charge per gram of the KS15 in the electrode.

In this electrolyte devoid of PC, the KS15 graphite exhibits approximately 330 mAh/g

30   reversible lithium capacity and about 73 mAh/g irreversible capacity (ie. the loss or difference in capacity between the 1st discharge and 1st recharge). Although a lower irreversible capacity is preferred, this anode/electrolyte combination is considered acceptable in practice (ie. is compatible).

Comparative Example 2

A laboratory coin cell was assembled and electrically tested as in Comparative Example 1 except that an electrolyte was employed which is not generally compatible with a lithiated graphite anode.

Again, the carbon powder used was KS15. This time, the electrolyte employed was 1 M $LiPF_6$ salt dissolved in a mixture of propylene carbonate (PC), EC, and DEC solvents in a volume ratio of 20/30/50 respectively.

Figure 3 depicts the voltage of the first 1½ cycles of this coin cell as a function of charge per gram of the KS15 graphite in the electrode.

In this PC containing electrolyte, the KS15 graphite electrode exhibits an unacceptably large irreversible capacity of about 400 mAh/g, of which about 300 mAh/g is evident in the voltage curve at about 0.7 V. The irreversible capacity is related to the amount of PC in the electrolyte. After much of the PC is consumed, the coin cell shows slightly deformed but reversible charge/discharge voltage curves. This electrolyte is thus incompatible with lithiated KS15 graphite.

Comparative Example 3

A laboratory coin cell was assembled and electrically tested as in Comparative Example 2 except that a different commercially available artificial flaky graphite was used as the electrode material, 5500 grade graphite (trademark of Superior Graphite Co.). (Cycle testing was also done at low rate, but this time at approximately C/20 rate.)

Figure 4 depicts the voltage of the first 1½ cycles of this coin cell as a function of charge per gram of the 5500 graphite in the electrode. As in Comparative Example 2, the 5500 graphite electrode exhibits an unacceptably large irreversible capacity at about 0.7 V in this PC containing electrolyte. This electrolyte is thus incompatible with lithiated 5500 graphite.

Inventive Example 1

A laboratory coin cell was assembled and electrically tested as in Comparative Example 2 except that boron treated KS15 graphite was used as the electrode material.

KS15 graphite powder was intimately mixed with B_2O_3 with an atomic ratio B/C of 2.0%. The mixture was then heat treated under flowing argon at 2200°C for 30 minutes, thereby producing boron treated KS15 graphite.

Figure 5 depicts the voltage of the first 1½ cycles of this coin cell as a function of charge per gram of the boron treated KS15 graphite in the electrode. Now, the irreversible capacity is markedly less than that observed in Comparative Example 2. The boron treated KS15 graphite electrode shows only about 95 mAh/g irreversible capacity loss on the first discharge and cycles well thereafter.

5   However, there is now a small but noticeable feature (ie. capacity plateau) at about 1.2 volts in the subsequent discharge and recharge cycles. Thus, the boron treated KS15 graphite differs from untreated KS15 in that the former shows some reversible lithium capacity at about 1.2 V versus Li/Li⁺.

The PC containing electrolyte appears compatible with this electrode.

10   **Inventive Example 2**

A laboratory coin cell was assembled and electrically tested as in Comparative Example 3 except that boron treated RG-5500 graphite (trademark of Superior Graphite Co.) was used as the electrode material, and the low rate cycling was performed at about C/40 rate.

15   The RG-5500 graphite powder provided is identified as being 5% B/C, but is apparently actually about 1.9% B/C according to the manufacturer.

Figure 6 depicts the voltage of the first 1½ cycles of this coin cell as a function of charge per gram of the boron treated RG-5500 graphite in the electrode. Again, the irreversible capacity is now markedly less than that observed in Comparative Example 3. The boron treated RG-5500 graphite

20   electrode shows only about 108 mAh/g irreversible capacity loss on the first discharge and cycles well thereafter. As in Inventive Example 1, there is now a small but noticeable feature at about 1.2 volts in the subsequent discharge and recharge cycles. Thus, the boron treated RG-5500 graphite differs from untreated 5500 graphite in that the former shows some reversible lithium capacity at about 1.2 V versus Li/Li⁺.

25   The PC containing electrolyte appears compatible with this electrode too.

Copper target X-ray diffraction profiles were obtained for the various graphitic carbonaceous electrodes used in the coin cells of Comparative Example 2, Comparative Example 3, Inventive Example 1, and Inventive Example 2. Figures 7a, b, c, and d show the respective profiles over the

30   range in 2θ between 40 to 60 degrees. Diffraction peaks for 3R rhombohedral phase graphite, if present, should be found at about 43.2°, 45.9°, and 56.4°. It was estimated that there was roughly 10% 3R rhombohedral phase in the untreated KS15 pattern of Comparative Example 2 (based on information given in the Journal of the Electrochemical Society, 143, No. 11, November 1996, p3466). Otherwise, it appeared that there was no rhombohedral phase present in any of the other samples (ie. boron treated

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KS15, 5500 graphite and RG-5500 graphite).

The d_{002} spacing for each of these samples was determined by Reitveld analysis of the x-ray diffraction profiles. Table 1 shows the d_{002} spacings for each sample along with B/C atomic ratio values. Both the KS15 and the 5500 graphites have been further graphitized by the boron treatment (as indicated by a reduction in the d_{002} spacing).

TABLE 1

Carbon material	B/C atomic ratio (% in mixture)	d_{002} spacing (in Å)
KS15 (Comp. Ex. 2)	0	3.3559
Boron treated KS15 (Inv. Ex. 1)	2.0	3.3553
5500 (Comp. Ex. 3)	0	3.3623
RG-5500 (Inv. Ex. 2)	? (actual 1.9 according to manufacturer)	3.3584

Illustrative Example 1

Various boron containing compounds are conventionally used to boron treat graphitic carbons in order to make them oxidation resistant. These compounds include B_2O_3, B_4C, and H_3BO_3. Additionally, all these compounds serve as graphitization catalysts, thereby making it easier to graphitize a given carbon. To illustrate this, varying amounts of these compounds were mixed with samples of one particular batch of spherical carbonaceous powder known as mesocarbon microbeads (MCMB) and were heat treated thereafter at 2650°C under argon gas for one hour. (MCMB is commonly employed as the active anode material in lithium ion batteries). Results are shown in Table 2 following.

All the boron compounds used resulted in greater graphitization than the control sample (which used no boron compound in the mixture). However, for a given B/C ratio (ie. 2%), different d_{002} values were obtained for each boron compound used.

TABLE 2

Boron compound used	B/C atomic ratio (% in mixture)	d_{002} spacing (in Å)
None	0	3.3704
B_2O_3	1	3.3658
B_2O_3	2	3.3636
B_4C	2	3.3609
H_3BO_3	2	3.3615

Illustrative Example 2

The reason that boron treatment can render a lithiated graphitic carbon compatible with an otherwise incompatible non-aqueous electrolyte is not understood. It had been speculated that the known oxidation resistant nature of prior art boron treated graphites might be associated with the advantages of the instant invention. P_2O_5 treatment of graphites is also known in the art as a means of preparing oxidation resistant graphite.

To determine if any oxidation resistant graphite might suffice, a laboratory coin cell was assembled and electrically tested as in Inventive Example 1 except that P_2O_5 treated KS15 graphite was used as the electrode material. Test electrode material was prepared by intimately mixing KS15 graphite powder with P_2O_5 in an atomic ratio P/C of 2.0%. The mixture was then heat treated under flowing argon at 1000°C for 30 minutes. P_2O_5 has a relatively low melting point and boiling point, so this lower temperature procedure is generally expected to give oxidation resistant graphite product.

Figure 8 depicts the voltage over the first 1½ cycles of this coin cell as a function of charge per gram of the graphite carbon electrode. The electrode is still incompatible with the electrolyte here, with the results being similar to that of Comparative Example 2. On this basis, it would appear that not all conventional oxidation resistant graphites provide the same benefits as the instant invention.

Those skilled in the art will be aware that the preceding disclosure discusses only some embodiments of the invention and that many other embodiments may be possible within the scope thereof. Accordingly, the scope of the invention should be construed by the following claims.

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WHAT IS CLAIMED IS:

1.   A non-aqueous lithium ion battery having a lithium insertion compound cathode and a non-aqueous electrolyte, the electrolyte including a lithium salt and a non-aqueous solvent, the non-aqueous solvent being compatible with a lithiated first graphitic carbon, the first graphitic carbon having an average d_{002} spacing more than 3.37 Å, and incompatible with a lithiated second graphitic carbon, the second graphitic carbon having an average d_{002} spacing less than 3.37 Å, wherein the improvement comprises a boron treated graphitic carbon anode having an average d_{002} spacing less than 3.37 Å.

2.   A non-aqueous lithium ion battery as claimed in claim 1 wherein the boron treated graphitic carbon is a flaky graphite.

3.   A non-aqueous lithium ion battery as claimed in claim 2 wherein the boron treated graphitic carbon is an artificial flaky graphite.

4.   A non-aqueous lithium ion battery as claimed in claim 1 wherein the crystalline structure of the boron treated graphitic carbon is less than 10% rhombohedral phase.

5.   A non-aqueous lithium ion battery as claimed in claim 4 wherein the crystalline structure of the boron treated graphitic carbon is essentially hexagonal phase.

6.   A non-aqueous lithium ion battery as claimed in claim 1 wherein the non-aqueous solvent is propylene carbonate.

7.   A non-aqueous lithium ion battery as claimed in claim 6 wherein the non-aqueous solvent additionally comprises ethylene carbonate and diethyl carbonate.

8.   A non-aqueous lithium ion battery as claimed in claim 6 wherein the lithium salt is $LiPF_6$.

9.   A non-aqueous lithium ion battery as claimed in claim 1 wherein the irreversible lithium capacity of the boron treated graphitic carbon anode is less than about 100 mAh/g.

10.   A non-aqueous lithium ion battery as claimed in claim 1 wherein the boron treated graphitic carbon anode is characterized by reversible lithium capacity at about 1.2 V versus Li/Li^+.

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11.   A non-aqueous lithium ion battery as claimed in claim 1 wherein the boron treated graphitic carbon anode comprises up to 2.3 atomic percent boron.

12.   A non-aqueous lithium ion battery comprising:

a lithium insertion compound cathode;

a non-aqueous electrolyte comprising a lithium salt and a non-aqueous solvent wherein the non-aqueous solvent is compatible with a lithiated first graphitic carbon, the first graphitic carbon having an average d_{002} spacing more than 3.37 Å, and is incompatible with a lithiated second graphitic carbon, the second graphitic carbon having an average d_{002} spacing less than 3.37 Å; and

a boron treated graphitic carbon anode having an average d_{002} spacing less than 3.37 Å which is prepared by heating a mixture of a carbonaceous compound and a boron containing compound under an inert atmosphere.

13.   A non-aqueous lithium ion battery as claimed in claim 12 wherein the carbonaceous compound has an average d_{002} spacing less than 3.37 Å.

14.   A non-aqueous lithium ion battery as claimed in claim 12 wherein the boron treated graphitic carbon anode has an average d_{002} spacing greater than 3.35 Å.

15.   A non-aqueous lithium ion battery as claimed in claim 12 wherein the carbonaceous compound is a flaky graphite.

16.   A non-aqueous lithium ion battery as claimed in claim 15 wherein the carbonaceous compound is an artificial flaky graphite.

17.   A non-aqueous lithium ion battery as claimed in claim 12 wherein the crystalline structure of the carbonaceous compound is less than 10% rhombohedral phase.

18.   A non-aqueous lithium ion battery as claimed in claim 17 wherein the crystalline structure of the carbonaceous compound is essentially hexagonal phase.

19.   A non-aqueous lithium ion battery as claimed in claim 12 wherein the boron containing compound is selected from the group consisting of B_2O_3, B_4C, and H_3BO_3.

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20. A non-aqueous lithium ion battery as claimed in claim 19 wherein the boron containing compound is B_2O_3.

21. A non-aqueous lithium ion battery as claimed in claim 12 wherein the atomic ratio of boron to carbon in the mixture is less than 0.05.

22. A non-aqueous lithium ion battery as claimed in claim 21 wherein the atomic ratio of boron to carbon in the mixture is between about 0.01 to 0.02.

23. A non-aqueous lithium ion battery as claimed in claim 12 wherein the mixture is heated at a temperature above about 2200°C.

24. A non-aqueous lithium ion battery as claimed in claim 12 wherein the mixture is heated for about 30 minutes.

25. A method of making a lithium ion battery, the battery including a lithium insertion compound cathode, a graphitic carbon anode having an average d_{002} spacing less than 3.37 Å, and a non-aqueous electrolyte including a lithium salt and a non-aqueous solvent wherein the non-aqueous solvent is compatible with a lithiated first graphitic carbon having an average d_{002} spacing more than 3.37 Å but is incompatible with a lithiated second graphitic carbon having an average d_{002} spacing less than 3.37 Å, the method comprising:

heating a mixture of a carbonaceous compound and a boron containing compound under an inert atmosphere to form said graphitic carbon anode.

26. A method as claimed in claim 25 wherein the carbonaceous compound is an artificial flaky graphite.

27. A method as claimed in claim 25 wherein the boron containing compound is selected from the group consisting of B_2O_3, B_4C, and H_3BO_3.

28. A method as claimed in claim 27 wherein the atomic ratio of boron to carbon in the mixture is between about 0.01 to 0.02.

29. A method as claimed in claim 25 wherein the non-aqueous solvent is propylene carbonate.
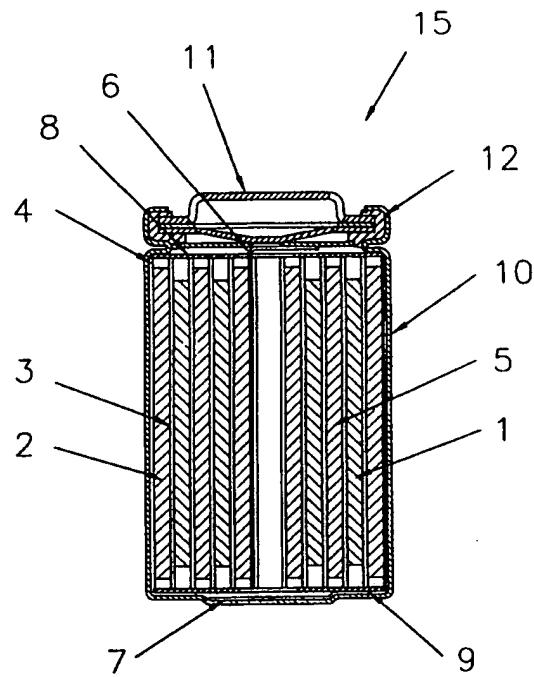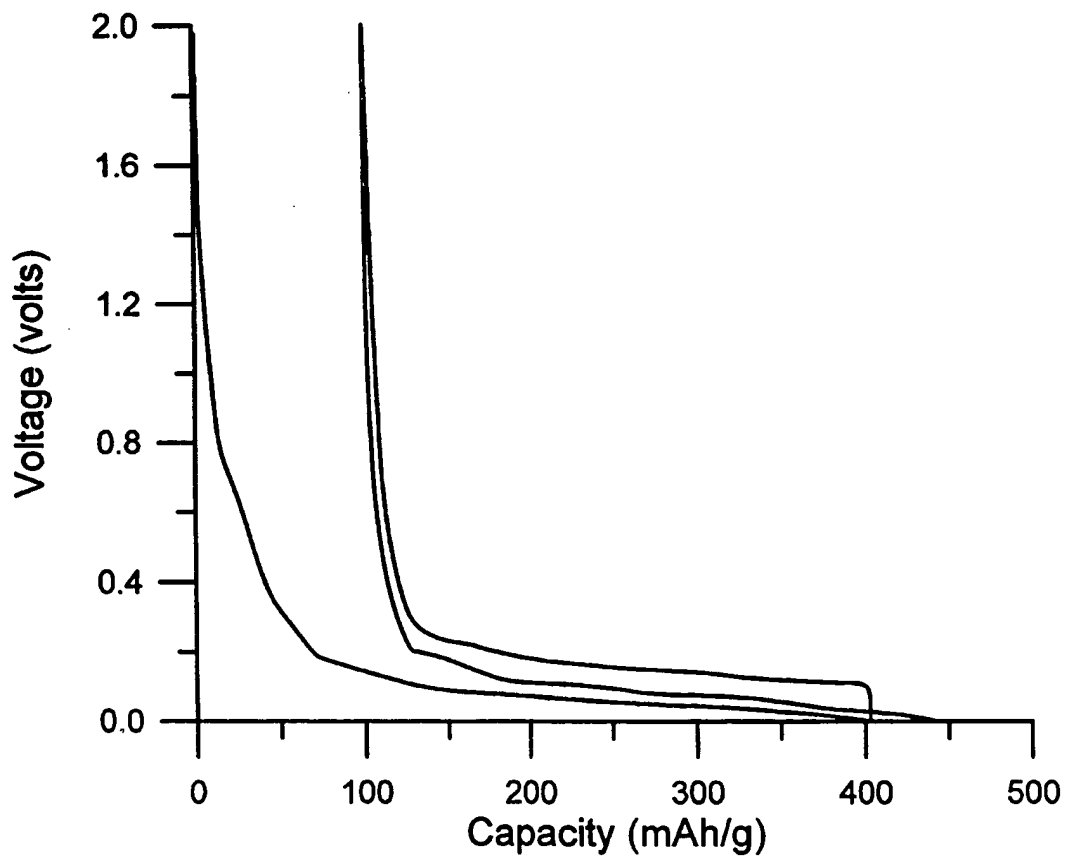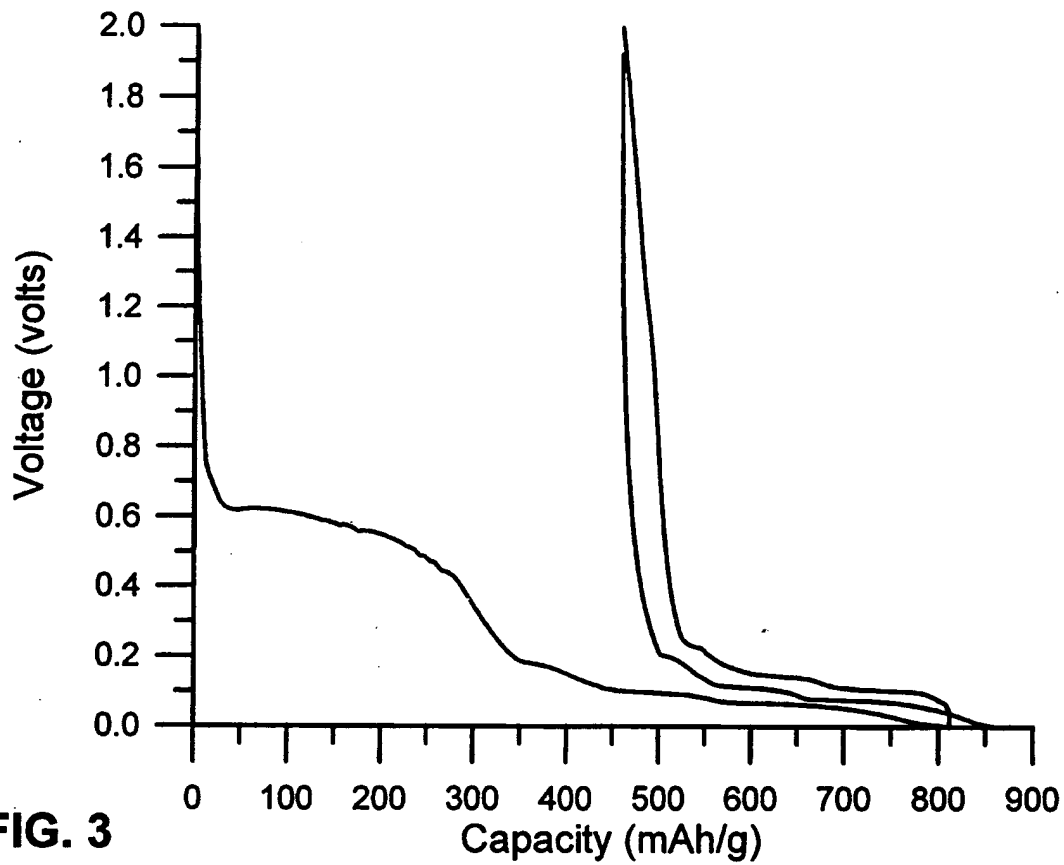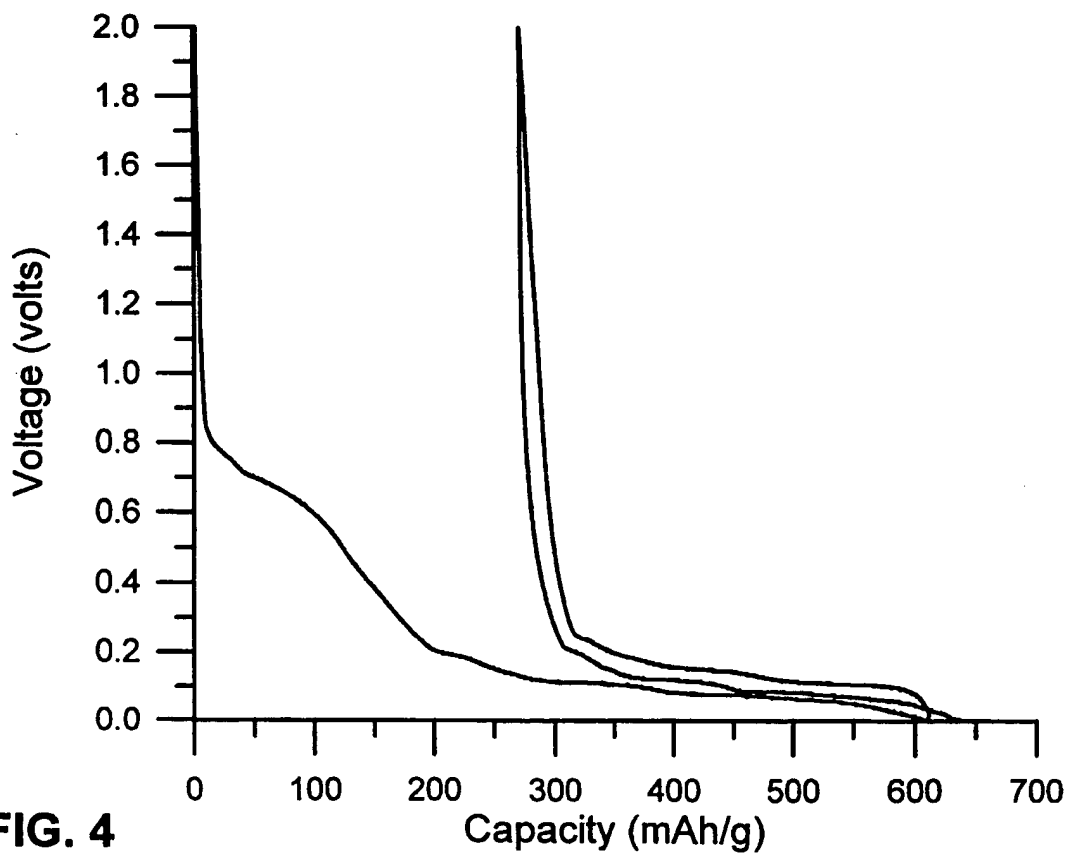
FIG. 1

FIG. 2

FIG. 3

Voltage (volts) vs Capacity (mAh/g)

FIG. 4

Voltage (volts) vs Capacity (mAh/g)

FIG. 5

Voltage (volts) vs Capacity (mAh/g)

FIG. 6

Voltage (volts) vs Capacity (mAh/g)

FIG. 7

FIG. 8